विध्न विचारत भीरु जन, नहीं आरम्भे काम, विपति देख छोड़े तुरंत मध्यम मन कर श्याम।
पुरुष सिंह संकल्प कर, सहते विपति अनेक, 'बना' न छोड़े ध्येय को, रघुबर राखे टेक।।

रचितः मानव धर्म प्रणेता

सद्गुरु श्री रणछोड़दासजी महाराज

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E A S

Q.1 From Pyrrole & any acyclic compounds prepare 3-(2-pyrrole)-propenoic acid.

Q.2 Prepare 4-bromo pyridine from pyridine.

Q.3 Give the structures & names of the products from the reaction of furfural, 2-furancarboxaldehyde with

(a) conc. aq. NaOH

(b) $CH_3-\overset{\overset{O}{\|}}{C}-CH_3$ / NaOEt

(c) $(CH_3CH_2CO)_2O + ACO^-Na^+$

(d) $PhCH_2CN / OH^-$

(e) cyclopentadiene / OH^- . Identify each reaction.

Q.4 From 2-methyl pyridine and any acyclic compound prepare :
$2\text{-}PyCOCH_3$ (Py indicates pyridine)

Q.5 From furfural prepare:

(a) Ethyl-5-bromo-2-furoate

(b) 1, 2, 5 tribromopentane.

Q.6 Give structures of the products from the following condensation :

(a) $P-CH_3C_6H_4CHO + (CH_3CH_2-\overset{\overset{O}{\|}}{C})_2O \xrightarrow{CH_3CH_2COO^-Na^+}$

(b) Cyclohexanone + $CH_3CH_2NO_2 + OH^- \longrightarrow$

(c) $C_6H_5CHO + PhCH_2C\equiv N \xrightarrow{OH^-}$

(d) Benzophenone + cyclopentadiene $\xrightarrow{OH^-}$

Q.7 Shows steps in the synthesis of :

(a) $P-NO_2C_6H_4CH_2OC_2H_5$

(b) $PhCH_2\overset{\overset{OCH_3}{|}}{C}H-CH_3$

(c) 2, 4- $(NO_2)_2\ C_6H_3-OC_3H_7$

Available starting materials are Ph – H, $Ph-CH_3$ & any alcohol of three or fewer carbon atoms.

Q.8 How can we convert

(i) $PhCH=CH-\overset{\overset{O}{\|}}{C}-CH_3$ to $PhCH=CHCO_2H$

(ii) $PhCH=CH-\overset{\overset{O}{\|}}{C}-CH_3 \longrightarrow PhCH=\overset{\overset{OH}{|}}{C}HCH-CH_3$

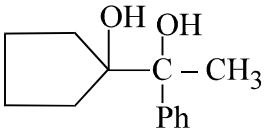
(iii) $PhCH=CH-\overset{\overset{O}{\|}}{C}-CH_3 \longrightarrow PhCH_2CH_2-\overset{\overset{O}{\|}}{C}-CH_3$

(iv) $PhCH=CH-\overset{\overset{O}{\|}}{C}-CH_3 \longrightarrow Ph-(CH_2)_3CH_3$

Q.9 Write structures for A through D given

$$PhH + CH_2 = CHCH_2OH \xrightarrow{HF} A \xrightarrow[(ii)\,H_2O_2/OH^-]{(i)\,BH_3/THF} B \xrightarrow{CrO_3/Py} C \xrightarrow[(ii)\,H_3O^{\oplus}]{(i)\,CN^-} D$$

Q.10 Give the product of the rearrangement of the cyclopentyl glycol E,



, and show how it is formed.

Q.11 Suggest a mechanism for the free radical oxidation of benzaldehyde, by atomspheric O_2. The reaction is initiated by a radical R° _____.

Q.12 Compound X, $C_9H_{10}O$ is inert to Br_2 in CCl_4 vigorous oxidation with hot alkaline permanganate yields benzoic acid. X gives a precipitate with semicarbazide hydrochloride & with 2,4 dinitrophenyl hydrozine (DNPH). Write all possible structures for X.

Q.13 Give the structures of A, B & C in $ICH_2CH_2CH_2 - Cl \xrightarrow[(ii)\,Ph_2S]{(i)\,AgBF_4} A \xrightarrow[Acetone]{NaH} B \xrightarrow{KOH} C$ is known as spiranyl epoxide.

Q.14 SynthesiseP-D-acetophenone (G) from benzene, aliphatic compounds & D_2O. The given sequence is, explain the mechanism & write the products:

$$Ph - H \xrightarrow{Br_2/Fe} A \xrightarrow{AC_2O/AlCl_3} B \xrightarrow[HCl]{MeOH} C \xrightarrow[(ii)\,D_2O]{(i)\,Mg/Et_2O} D \xrightarrow{H_3O^{\oplus}} E$$

Q.15 Synthesise :

(a) $Ph - H \longrightarrow P - NO_2\ C_6H_4\ CO_2H$

(b) $Ph - H \longrightarrow$ adipic acid

Q.16 Convert :

(a) $Ph - H \longrightarrow P - HOOC - C_6H_4 - CH_2CO_2H$

(b) $Ph - H \longrightarrow$ 1, 2, 4-benzene tricarboxylic acid

(c) $Ph - H \longrightarrow$ 2-methyl-5-chloro benzoic acid

(d) $Ph - H \longrightarrow$ 2-bromo-4-nitrobenzoic acid

Instruction $\longrightarrow$ Do not repeat the preparation of any needed intermediate product.

Q.17 Use naphthalene to synthesise -2- Naphthoic acid.

Q.18 Prepare adipic acid & succinic acid from THF.

Q.19 Prepare 6-oxo-6-phenyl hexanoic acid from cyclohexanol & C_6H_6.

Q.20 Account for the fact that

(a) maleic acid is a stronger acid than fumaric acid but maleate, monoanion is a weaker acid than furmarate monioanion &

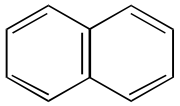
(b) Phthalic acid is stronger than either isophthalic or for phthalic acids but phthalate monoanion is weaker than isophthalate & terphthalate monoanions.

Q.21 Synthesise :

(a) $PhCH_2\ CH_2\ CO_2H$ from $Ph\ CH_2CH_2\ Br$ with in 2 step.

(b) With the acid of simple chemical tests differentiate among 2-chloropropanoic acid, pyruvic acid, acrylic acid & propanoic acid.

Q.22 Prepare benzilic acid(1–hydroxy –1, 1–diphenyl ethanoic acid) from either cis-or trans-stilbene within 3 steps.

Q.23 Use Ph – H, Ph Me, Xeylenes, NaPH & DEM to prepare :[Nap → ]

(a) $Ph\ CH_2\ CH_2\ CH_2\ CH_2\ COOH$

(b) $P - HOOC - C_6H_4\ CH_2\ CH_2\ COOH$

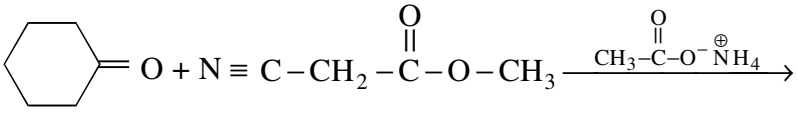
(c) $P - HOOC - CH_2\ CH_2\ C_6H_4 - CH_2CH_2\ COOH$

(d) α –Nap – $CH_2\ CH_2\ COOH$

(e) β – Nap $CH_2\ CH_2\ COOH$

Q.24 Convert DEM to 2-oxobutanoic acid

Q.25 Give the structures of the products from the following condensations :

(a) 

(b) Benzophenone + cyclopentadiene $\xrightarrow{\bar{O}H}$

(c) Outline the steps in the base catalysed self - condensation of a typical nitrile $CH_3\ CH_2\ CN$.

Q.26 Convert Ph – H and any aliphatic compound to 2– (2, 4-dinitrophenyl) propanoic acid (D).

Q.27 Provide structures for the products of the reaction of $Ph\overset{+}{N}_2$ with

(a) $PhNMe_2$

(b) 2-naphthol

(c) $Ph - CH_3$

Q.28 Prepare sodium P-dimethylaminoazobenzene sulphate, methylorange (a), from appropriate amines.

(b) Explain, with structures, why methylorange is an acid-base indicators.

Q.29 In the vilsmeier reaction, an aromatic 3° amine ($ArNR_2$) undergoes electrophilic substitution with Me_2NCHO (-dimethyl- formamide) & $POCl_3$.

(a) Give the product of the reaction with $PhNMe_2$.

(b) Outline the steps in the reaction in (a) showing the electrophile.

Q.30 Synthesise from NaPH, & any other reagent

(a) β-$NpNH_2$ by three methods.

(b) $2\text{-}NPCH_2NH_2$

(c) Naphthionic acid (4-amino-1-naphthalene sulfonic acid)

(d) 1, 2-dinitronaphthalene.

Q.31 $CHCl_3 + EtO^-\ Na^+ \longrightarrow A \xrightarrow{EtOH} B \xrightarrow{2EtO^-} C \xrightarrow{\text{excess of } CH_3MgBr} D \xrightarrow[CH_3CO_2H]{H_2CrO_4} E$. The colour of the solution becomes green.

'C' is known as " ethylortho formate".

Q.32 Devise a synthesis of $Ph - \overset{O}{\overset{\|}{C}} - CH_3$ from $Ph - \overset{O}{\overset{\|}{C}} - Cl$ & DEM. You have available

(i) NaH / THF

(ii) H_2O / H_2SO_4

Can this synthesis be a general method for preparing methyl Ketone.

Q.33 Prepane $(n - C_4H_9)_3\ C - CO_2H$ from 1-bromopentane & 1- bromobutane.

Q.34 Identify A to E in the following reactions & explain the mechanism.

$$Ph - SO_2Cl + EtNH_2 \longrightarrow A \xrightarrow{NaOH} B \xrightarrow{EtBr} C \xrightarrow{H_3O^{\oplus}} D + E.$$

Q.35 An aromatic hydrocarbon (A) of the formula C_8H_{10} on oxidation with acidified $KMnO_4$ produced a dicarboxylic acid (B) having C = 57.8% and H = 3.6%. The silver salt of the acid contains 56.8% Ag. The acid does not form anhydride on heating, but on nitration with conc. HNO_3 and conc. H_2SO_4 gave only one mononitro derivative (C). The acid (B) on heating with soda-lime gives benzene. What are (A), (B) and (C)?

Q.36 An organic compound (A), C_8H_{10}, yields on oxidation a dibasic acid (B), $C_8H_6O_4$, which on heating produces an anhydride (C), $C_8H_4O_3$. Acid (B) on nitration produces two mononitro derivatives (D) and (E), both on heating with soda-lime produced nitrobenzene, while acid (B) on distillation with soda-lime produced benzene. What are (A) to (E)?

Q.37 Compound (A), C_8H_9Cl, on treatment with aqueous KOH gives (B), $C_8H_{10}O$, which gives a red colour with ceric ammonium nitrate and evolve H_2 on reaction with Na. Compound (B) either on oxidation or catalytic hydrogenation in presence of copper gives (C), which forms an oxime and cyanohydrin and also give positive iodoform test. What are (A), (B) and (C)? Also show the action of EtO^-K^+ on (A), write down all the possible isomers of (A).

Q.38 An organic compound (A), $C_9H_{10}Br_2$ gives (B), $C_9H_{11}OBr$ on reaction with hot alcoholic KOH solution. Compound (B) is resistant to further action of alkali. (B) on heating with conc. H_2SO_4 undergoes dehydration to give (C), which on ozonolysis gives ethanal and another compound (D). Compound (D) forms a phenyl hydrazone with $C_6H_5NHNH_2$ and gives positive Tollen's test, but does not give red ppt. with Fehling's reagent. It on heating with acetic anhydride and sodium acetate produced o-bromocinnamic acid. What are compound (A) to (D)? Explain all the reactions involved.

Q.39 An anomatic hydrocvarbon (A), C_7H_8 on reaction with Cl_2 in the presence of halogen carrier at low temp. give two compounds (B) and (C) of formula C_7H_7Cl. Both the compounds on treatment with Cl_2 in absence of catalyst produced two compounds of the formula, $C_7H_6Cl_2$, i.e. (D) and (E). Both (D) and (E) on treatment with KCN followed by hydrolysis produced two acids (F) and (G) of formula, $C_8H_7O_2Cl$. Both the acids on heating with dilute HNO_3 get oxidised into two acids (H) and (I) of formula, $C_7H_5O_2Cl$. Both these acids on heating with soda-lime produced a single compound chlorobenzene. What are compounds (A) to (I)? Give balanced equations for the reactions.

Q.40 (A) and (B) are two isomers of molecular formula C_8H_{10}. Both on oxidation gave a monobasic and a dibasic acid respectively. The latter compound on heating eliminates one mole of H_2O to give cyclic anhydride, while the former on treatment with $LiAlH_4$ gave (C), which on heating with Cu at 300°C produced (D), which gave positive test with Schiff's reagent and Tollen's reagent. It on heating with acetic anhydride and sodium acetate givs cinnamic acid. What are compounds (A) to (D)? Explain the reactions giving equations.

Q.41 A hydrocarbon (A), C_9H_{10}, adds one mol of Br_2 to give (B), $C_9H_{10}Br_2$. Hydrolysis of (B) gives (C), $C_9H_{12}O_2$. Oxidation of (C) gave two acids identified as benzoic acid and acetic acids. Ozonization of (A) followed by hydrolysis in absence of Zn also produced the same acids. What are (A) to (C)? Explain these reactions. Are (B) and (C) optically active, if so, how many isomers of each are possible?

Q.42 An organic compound (A), C_9H_{12} gave (B), $C_8H_6O_4$ on oxidation by alkaline $KMnO_4$. (B) on heating does not form anhydride. Also (B) reacts with Br_2 in presence of Fe to give only one monobromo derivative (C), $C_8H_5BrO_4$. What are (A), (B) and (C)?

Q.43 The compound C_8H_9Cl, (A), on treatment with KCN followed by hydrolysis gives $C_9H_{10}O_2$ (B). Ammonium salt of (B) on dry distillation yields (C), which reacts with alkaline solution of bromine to give $C_8H_{11}N$. (D). Another compound (E),($C_8H_{10}O$) is obtained by the action of HNO_2 on (D) or by the action of aqueous potash on (A). (E), on oxidation gives (F) ($C_8H_6O_4$), which gives the inner anhydride (G) on heating. Deduce the structures of (A) to (G) giving the reactions involved.

Q.44 An aromatic hydrocarbon (A) containing 91.35% carbon gives on chlorination three isomeric monochloro derivatives 'X', 'Y' and 'Z'. % of chlorine in each one of these is 28%. On oxidation with $KMnO_4$ all the three give one monobasic acid. Acid obtained from'X' gives benzene on distillation with soda-lime. Acids obtained from Y and Z on similar treatment give monochloro benzene. Determine the structural formula of varius compounds and explain the reactions involved.

Q.45 An aromatic hydrocarbon (A) has vapour density 46. On oxidation with chromyl chloride in CCl_4 it gives compound (B), which on reaction with conc. NaOH solution produced an aromatic acid (C) and an alcohol (D). Acid (C) can also be obtained by the oxidation of (A) with alkaline $KMnO_4$. Compound (D) is obtained when (B) is reduced with Na – Hg and an acid. (D) can also be obtained by the reduction of acid (C) by means of $LiAlH_4$. Explain the reactions involved and the structural formulae of (A), (B), (C) and (D)?

Q.46 An organic compound containing C, H and O exists in two isomeric forms (A) and (B). 0.108 g of an isomer gives on combustion 0.308 g of CO_2 and 0.072 g of H_2O. (A) is insoluble in NaOH and $NaHCO_3$, while (B) is soluble in NaOH. A reacts with conc. HI to give compound (C) and (D). (C) can be separated from (D) by the ethanolic $AgNO_3$ solution and (D) is soluble in NaOH. (B) reacts readily with bromine to give compound (E) of formula, $C_7H_5OBr_3$. Identify (A) to (E).

Q.47 A mixture of two aromatic compounds (A) and (B) was separated by dissolving in $CHCl_3$ followed by extraction with aq. KOH solution. The organic layer containing compound (A), when heated with alcoholic solution of KOH produced a compound (C), C_7H_5N associated with an unpleasent odour. The alkaline aqueous layer onthe other hand, when heated with $CHCl_3$ andthen acidified gave a mixture of two isomeric compounds (D) and (E) of molecular formula $C_7H_6O_2$. Identify the compounds (A) to (E).

Q.48 An organic compound (A) contains 69.42 % C, 5.78 % H and 11.57 % N. Its vapour density is 60.50. It evolves NH_3 when boiled with KOH. On heating with P_2O_5, it gives a compound (B) containing 81.55 % C, 4.85 % H and 13.59 % N. On reduction with Na and C_2H_5OH (B) gives a base, which reacts with HNO_2 giving off N_2 and yielding an alcohol (C), which can be oxidised to benzoic acid. What are (A) to (C)? Explain the reactions involved.

Q.49 An organic compound has 76.6 % carbon and 6.38% hydrogen. Its V.D. is 47. It gives characteristic colour with $FeCl_3$ solution. The compound (A) when treated with CO_2 and NaOH at 140°C under pressure gives (B), which on acidification gives (C). The compound (C) reacts with acetyl chloride to give (D), which is a well known pain killer. Identify (A), (B), (C) and (D) and explain the reactions involved.

Q.50 On ozonolysis (X), $C_{18}H_{20}O$, gives $C_{10}H_{12}O$ (A) and $C_8H_8O_2$ (B). Compound (A) gives the iodoform test and with NH_2OH gives the oxime $C_{10}H_{13}ON$ (C). The oxime undergoes rearrangement to give an amide when treated with PCl_5 in dry ether. The amide on hydrolysis gives CH_3COOH and a compound $C_8H_{11}N$ (D). Compound (D) with HNO_2 at 0°C gives an aromatic alocohol $C_8H_{10}O$, oxidation of which gives phthalic acid. (B) on mild oxidation gives a carboxylic acid, $C_8H_8O_3$, which is degraded by HI to CH_3I and p-hydroxy benzoic acid. Identify the compound (X) and give the reactions involved.

